IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of Rakowski   :

Group Art Unit 1742   :   OXIDATION RESISTANT FERRITIC
                                         :   STAINLESS STEELS
Serial No. 10/654,203   :
                                         :   Confirmation No. 5809
Filed September 3, 2003   :
                                         :
Examiner Jessee Roe   :

DECLARATION OF MICHAEL P. BRADY

Pittsburgh, Pennsylvania 15222-2312
August 23, 2007

Commissioner for Patents
P.O. Box 1450
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Sir:

1.   I, Michael P. Brady, declare as follows:

2.   I am a citizen of the United States and currently reside at 110 Clemson Drive, Oak Ridge, TN 37830.

3.   I am over the age of eighteen and am competent to make the statements in this Declaration.

4.   I received a Ph.D. degree in Materials Science and Engineering from the University of Florida in August , 1993.

5.   During 1993-1997, I was a National Research Council Postdoctoral Fellow at NASA's Glenn Research Center in the Environmental Durability Branch of the Materials Division and pursued research in high temperature alloy design and oxidation. In 1997, I joined the Materials Science and Technology Division at Oak Ridge National Laboratory as an ORISE Postdoctoral Fellow. I became a full time R&D staff member

at ORNL in 1998, and was promoted to Senior R&D staff in 2004. I am currently pursuing research in the development of corrosion-resistant, high temperature materials for cleaner and more efficient energy conversion and combustion systems, and the use of corrosion reactions to synthesize functional services for improved energy-related electrochemical systems and devices such as fuel cells. In fiscal year 2007, I am the lead/co-principle investigator for over $3 million of research activities.

6.   I am the author/coauthor of 5 issued U.S. Patents, 8 Pending U.S. Patents or ORNL Invention Disclosures, and over 80 publications in the areas of oxidation, alloy design, fuel cells, and coatings. Approximately half of my patents/invention disclosures and are in the area of stainless steels, with 3 specifically directed to fuel cell issues. I am the author/coauthor of more than 15 archival journal articles specifically in the areas of stainless steels or fuel cells, including a recent paper on alumina-forming stainless steels in the international multidisciplinary journal *Science*, as well as specialty publications in leading metallurgical journals such as *Oxidation of Metals, Scripta Materialia, Journal of Power Sources, Metallurgical and Materials Transactions,* and *International Journal of Hydrogen Energy.* I also serve on the international advisory board of the journal Oxidation of Metals, and act as a technical reviewer for virtually every major metallurgical related journal.

7.   I have specifically led efforts devoted to the evaluation and development of ferritic stainless steels (and related alloys) for SOFC fuel cells. I have conducted oxidation studies of ferritic stainless steels, as well as austenitic, Ni-base, Cr-base, and intermetallic alloys. I am well versed in surface preparation methods, including mechanical abrasion and electropolishing.

8.   I have thoroughly reviewed U.S. Patent Application Serial No. 10/654,203 to Rakowski (the "Rakowski application"). The Rakowski application describes a method of electrochemically modifying a surface of a ferritic stainless steel to improve the oxidation resistance of the surface when exposed to high temperature, oxidizing environments, such as the environment within a solid oxide fuel cell ("SOFC"). Electropolishing is a well known method of electrochemically modifying a steel surface and operates by removing material from the surface to flatten (smooth) the surface. A

benefit of electropolishing is that the smoothed surface better reflects light and, therefore, the appearance of the surface is improved. It can also be used to minimize surface defects to improve other properties such as fatigue resistance. I am not aware of any previous findings of electropolishing enhancing high temperature oxidation resistance.

9. At a time just prior to September 3, 2003, metallurgists conventionally believed that the high temperature oxidation resistance of a ferritic stainless steel surface, as well as other classes of high temperature alloys, would not be improved by electropolishing the surface. Instead, metallurgists conventionally believed that mechanically deforming (roughening) the surface of a stainless steel would introduce cold work and dislocations, resulting in a fine local surface grain size on heating to high temperatures, that would generally improve oxidation resistance by increasing outward diffusion of the protective scale forming element (typically Cr or Al). It was believed that highly polished surfaces, either by mechanical polishing or electropolishing, result in a low defect surface microstructure, which does not recrystallize to a fine local grain size and therefore does not provide preferential outward diffusion paths to enhance protective oxide scale formation. It is general practice in the oxidation research community to perform oxidation tests with mechanically abraded surfaces, typically in the 600 grit surface finish range. The conventional beliefs regarding surface roughness, grain size refinement, and oxidation resistance in alloys have been prevalent for decades, for example refer to the references C. S. Giggins et al., "The Effect of Alloy Grain-Size and Surface Deformation on the Selective Oxidation of Chromium in Ni-Cr Alloys at Temperatures of 900°C and 1000°C", 245 Transactions of the Metallurgical Society of AIME at 2509-2514 (December 1969); and J. M. Rakowski et al., "The Effect of Surface Preparation on the Oxidation Behavior of Gamma TiAl-Base Intermetallic Alloys", 35 Scripta Materialia at 1417-1422 (1996). Both of these references suggest the advantage of a mechanically deformed surface in regards to establishing the desired continuous, protective oxide surface scale (chromia or alumina) to enhance oxidation resistance.

10. In light of the conventional beliefs regarding electropolishing discussed in paragraph 9 above, I was very surprised by the unexpected oxidation test results

described in the Rakowski application. The Rakowski application describes testing wherein the oxidation resistance of certain ferritic stainless steels was significantly improved by electropolishing surfaces of the steel, and also was improved relative to samples of the steel processed to have relatively rough surfaces. I believe that the results described in Rakowski were entirely unexpected prior to September 3, 2003, and were directly opposite to what a metallurgist would have predicted at that time based on the conventional beliefs in the field, described in paragraph 9 above. At a time just prior to September 3, 2003, metallurgists would have predicted that ferritic stainless steel surfaces that were electropolished would exhibit no beneficial oxidation-related effects, and likely a reduced level of oxidation resistance.

11.   I believe that the results described in the Rakowski application are significant in that the inventor discovered that electropolishing provides a ready technique for further enhancing the oxidation resistance of surfaces of certain ferritic stainless steels.

12.   I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or document or any registration resulting therefrom.

Date: 8/23/07   Michael P Brady

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THE EFFECT OF SURFACE PREPARATION ON THE OXIDATION BEHAVIOR OF GAMMA TiAl–BASE INTERMETALLIC ALLOYS

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Introduction

Titanium aluminides, specifically the intermetallic compound gamma TiAl, are being investigated as potential aerospace and automotive materials due to high specific strength and stiffness (1–6). The oxidation behavior of gamma TiAl has been studied extensively (7–22). Oxygen exposures tend to produce slow growing alumina rich scales at low temperatures. At higher temperatures (approximately 800°C), the alumina breaks down locally and mixed oxide nodules form. At temperatures at and above 1000°C, the nodules grow rapidly and merge to form a thick mixed oxide scale. The oxidation behavior in atmospheres containing nitrogen is significantly different. Nitrogen reacts with titanium in the alloy to form titanium nitrides at the scale/alloy interface. The result is a discontinuous layer of aluminum oxide particles at the scale/alloy interface. It is not possible to form a continuous, protective alumina layer, resulting in rapid oxidation in air. Important initial research also pointed to surface preparation as a potential factor in the oxidation behavior of gamma TiAl alloys (23).

The material used for this study was stoichiometric Ti–50Al (nominal composition in atomic percent), a single phase γ TiAl alloy with large equiaxed grains. In addition, material with a lower aluminum content (Ti–48Al) was also investigated. This alloy is notable because it contains significant amounts of the intermetallic alpha–2 Ti_3Al dispersed in small lamellar colonies as a second phase.

Experimental Procedure

Oxidation specimens were prepared by cutting on a low speed diamond saw and then grinding through 600 grit SiC paper. Thermogravimetric analysis (TGA) was used to record continuous mass change as a function of time at elevated temperatures during exposure to a controlled atmosphere. Selected specimens were then polished with 1 micron diamond paste. X-ray diffraction analysis of oxide scales was performed with a Philips diffractometer in both normal and glancing angle (1°) modes. Morphological

analysis was carried out on a JEOL 35CF SEM equipped with EDS and WDS. A face–to–face mounting technique was employed to fabricate cross–section TEM specimens, which were thinned to electron transparency by dimpling and subsequent ion milling on a Gatan PIPS mill at a 4° angle of incidence. Transmission electron microscopy was performed primarily on a JEOL 2000FX equipped with a light element EDS system.

Results and Discussion

600 Grit Surface Finish

Exposure to oxygen results in small weight gains due to oxygen uptake at temperatures lower than 800°C for specimens prepared to 600 grit. The scale which forms is rich in alumina and transport through it is slow. The weight gain increases at 900°C due to the formation of mixed oxide nodules, which are locally thicker regions of the scale consisting of a mixture of rutile TiO_2 and alumina (Fig. 1). Transport across the scale is more rapid due to the partition of cross–sectional areas into regions of slow transport through alumina and rapid transport through nodules, as can be noted from surface scanning electron micrographs (Fig. 2). A set of short time exposures in oxygen proved that nodules form specifically at sites of alpha–2 in the microstructure for exposures of the Ti–48Al alloy (Fig. 3). After thirty minutes, the alpha–2 lamellae are decorated with thick oxide, while the surrounding gamma grains form a thin alumina film. A two hour exposure results in the formation of nodules at the lamellae sites. After five hours, the lamellar regions are completely consumed by mixed oxide nodules, which cease to grow past the boundaries of the alpha–2 colonies, as verified by 180 and 360 hour experiments. At 1000°C the weight gain increases by an order of magnitude due to sudden rapid growth and merging of nodules (Fig. 4). A thick mixed scale forms and diffusion through rutile TiO_2 is dominant. It is not known why the nodules suddenly break free. It is possible that the ternary oxide $TiAl_2O_5$ forms, but the equilibrium transformation temperature for the reaction between TiO_2 and Al_2O_3 is 1100°C (24). Exposure to air at high temperatures results in larger mass gains at all temperatures when compared to corresponding oxygen exposures, as can be noted from the oxidation kinetics (Fig. 5). The scale forms in a homogeneous manner, and the final product is similar to the scale formed at 1000°C in oxygen. This is caused by the formation of titanium nitrides at the scale/alloy interface, which oxidize to titanium oxide and prevent the scale from becoming continuous (25–26).
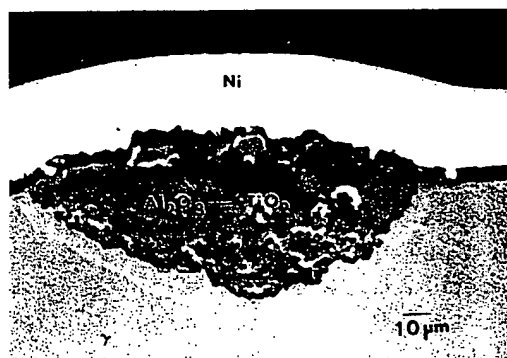

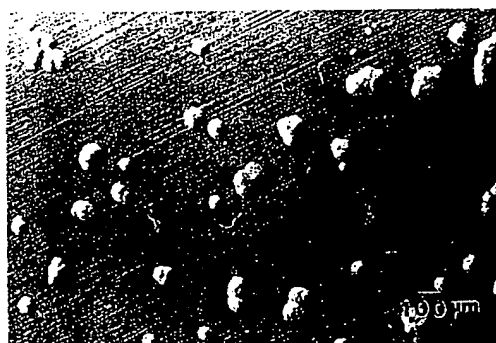Figure 1. Cross–section SEM micrograph, Ti–50Al, 600 grit surface finish, 1 week, 900°C, oxygen.

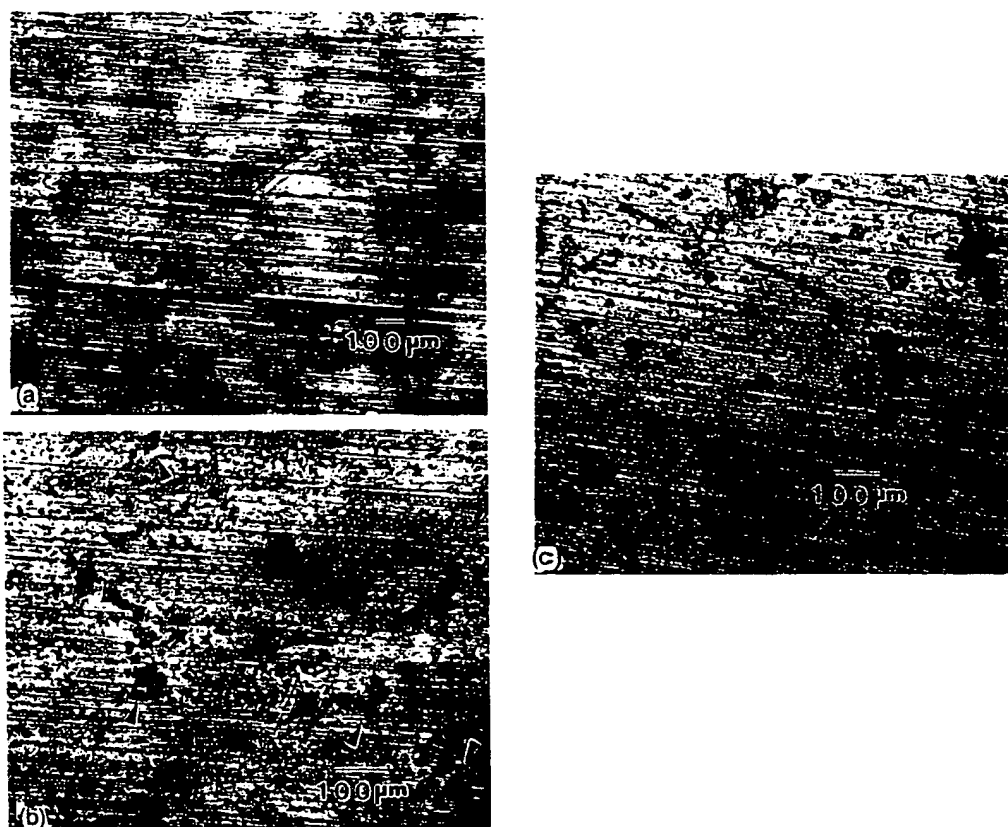Figure 2. Surface SEM micrograph, Ti–50Al, 600 grit surface finish, 1 week, 900°C, oxygen.

Figure 3. Surface optical micrographs, Ti–48Al, 600 grit surface finish, 900°C, oxygen. a) 30 minutes; b) 2 hours; c) 5 hours.

1 Micron Surface Finish

Specimens polished to 1 μm exhibit accelerated oxidation in pure oxygen with respect to specimens finished to 600 grit. The weight gain of the 1 μm finished specimen is comparable an air exposure at the same temperature (Fig. 5). A thick mixed scale forms, rather than a typical alumina film broken sporadically by mixed oxide nodules. Variations in surface finish were found to have no effect in an air atmosphere. The parabolic rate constants as well as the activation energy obtained by plotting these constants versus 1/T for the air exposures, 1 μm surface finish oxygen exposures, and 1000°C 600 grit surface finish oxygen exposures all are similar to that for diffusion in rutile TiO_2. The consistent reduction in the parabolic rate constant compared to a perfect rutile former is due to the formation of alumina in the scale, which reduces the effective rutile diffusion cross–sectional area. This increases the diffusion distance and reduces the oxidation rate somewhat. Lower temperature 600 grit oxygen exposures result in oxidation kinetics approaching those for alumina growth.

Oxidized specimens with both 600 grit and 1 μm surface finishes were examined in cross–section with transmission electron microscopy. Both specimens formed a titanium–rich phase with a lattice parameter of 6.9Å and cubic symmetry. The diffraction patterns from this phase do not match any relevant phases known for the Ti–Al–O–N system. Dowling and Donlon first reported the existence of this phase and the lattice parameter (27). Zheng et al. have recently published X–ray diffraction data which is consistent with the work of Dowling and Donlon (28). Convergent beam electron diffraction analysis reveal a cubic phase with either the P432 or $P4_232$ space group (29). The major difference
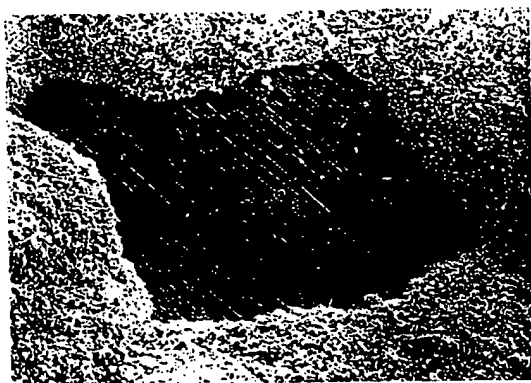
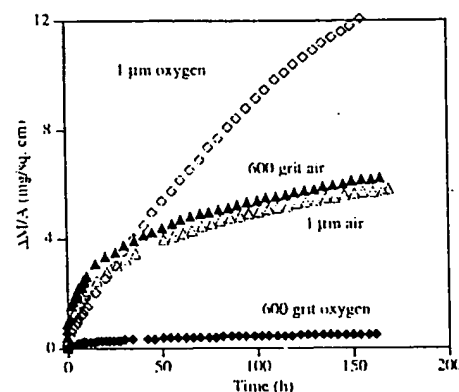Figure 4. Surface SEM micrograph, Ti–50Al, 1 week, 1000°C, oxygen.

Figure 5. TGA data for Ti–50Al; air and oxygen exposures, 600 grit and 1 μm specimens, 900°C.

between the two specimens is that the one with a 600 grit surface finish exhibits a recrystallized gamma TiAl zone within the alloy, which formed during the early stages of oxidation (less than 1 hour) (Fig. 6). Specimens with a 1 micron finish do not exhibit this recrystallized gamma layer (Fig. 7). Similar effects have been observed in the nickel–chromium system by Giggins and Pettit (30). Compared to the unexposed alloy, which has an approximate grain size of 100 microns, the grain size of the recrystallized grains is quite small. The introduction of this layer increases the grain boundary area near the specimen surface by a large amount.

Conclusions

Parabolic rate constant analysis confirms that rapid oxidation of gamma TiAl corresponds to rutile TiO_2 formation. It is established that air exposures result in the nitrogen effect, causing titanium nitride formation and subsequent rutile–dominated oxidation kinetics. When rutile forming kinetics dominate, the system is close to a maximum rate of oxidation. Therefore, surface finish is irrelevant in air, as the effect cannot drive the system to oxidize any faster. In oxygen, the rate is between that for alumina and rutile formation for abraded surfaces, indicating a primarily alumina scale. With a finely polished surface or very high temperatures, the oxidation rate increases several orders of magnitude, corresponding to mainly rutile formation. Once again, the material has reached a maximum oxidation rate for the temperature considered. Recent work by Becker, et al., reports a higher oxidation rate in oxygen compared to air at 900°C, with the opposite occurring at 1000°C (7). This inconsistent result can be explained by noting that the samples investigated were polished with 4000 grit SiC paper, which is significantly finer than the 600 grit paper used in this study and others. At 900°C, the effect of surface finish leads to more rapid oxidation in oxygen. At 1000°C, the effect of surface finish is masked by overall rapid oxidation due to nodule growth.

The variation of oxidation behavior of gamma TiAl in oxygen seems to be a direct consequence of the formation of a recrystallized zone within the alloy as a result of energy stored by near–surface deformation induced by the grinding process. The recrystallization promotes the formation of an alumina film in oxygen. Such an effect is not unknown in other alloy systems. Giggins and Pettit observed a similar phenomenon in the Ni–Cr system (30). The gamma alloys studied possess coarse grain size. Recrystallization results in the addition of many grain boundaries. It is likely that this layer is enhancing diffusion via short circuits within the alloy, increasing the diffusivity of species to the scale/alloy interface. Increasing the aluminum diffusivity in the alloy would result in stability of aluminum oxide
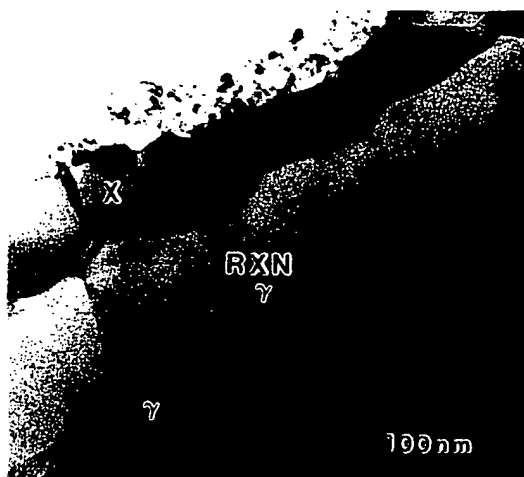
Figure 6. xTEM micrograph, Ti–50Al, 1 hour, 900°C, oxygen, 600 grit surface finish.
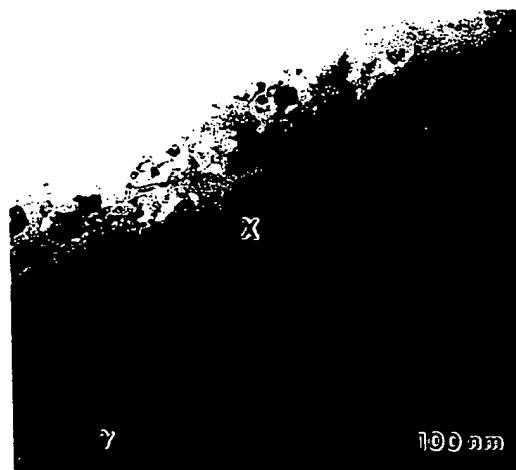

Figure 7. xTEM micrograph, Ti–50Al, 1 hour, 900°C, oxygen, 1 μm surface finish.

at lower aluminum content by reducing aluminum depletion/titanium enrichment. Another possibility is that the high dislocation density at the surface of the abraded specimen may provide another short circuit path. However, the recrystallized layer forms within five minutes, so dislocations would only play a role in the earliest stage of oxidation before they are eliminated by recrystallization.

The surface finish effect does not exist in air. A different oxidation mechanism is operative, with the nitrogen effect precluding the formation of an alumina layer. Enhanced substrate diffusion plays little or no role in increasing the oxidation resistance. However, recent research has indicated that at lower temperatures (600°C), TiAl alloys no longer react with nitrogen (31). The surface finish may then play a role in both air and oxygen atmospheres.

In the future, work in this area will concentrate on examination of both unexposed and very short time exposure cross–sections. Examination of the near–surface regions of unexposed specimens will serve to characterize the induced deformation with respect to bulk material before any transformation due to oxidation occurs. The very short time exposures are needed to characterize the initial stages of recrystallization, i.e. nucleation sites and reaction kinetics.

Acknowledgments

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The Effect of Alloy Grain-Size and Surface Deformation on the Selective Oxidation of Chromium in Ni-Cr Alloys at Temperatures of 900° and 1100° C

C. S. Giggins and F. S. Pettit

The oxidation properties of Ni-Cr alloys with fine grains, coarse grains, and deformed surface layers have been studied at temperatures of 900° and 1100°C in 0.1 atm of oxygen. The oxidation rates of alloys containing between 10 and 30 wt pct Cr have been found to be dependent upon the grain size of the alloy. Fine-grained alloys had smaller oxidation rates than coarse-grained alloys because of the selective oxidation of chromium at alloy grain boundaries. In this compositional range alloys with deformed surface layers behaved similar to fine-grained alloys due to recrystallization of the deformed surface layer.

I_N the preceding paper[1] it was found that during the oxidation of Ni-Cr alloys, the volume fraction of precipitated Cr_2O_3 could be greater at alloy grain boundaries than at other areas of the alloy surface. In the case of alloys with chromium concentrations equal to or greater than 30 pct,* the volume fraction of Cr_2O_3

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*All compositions are given as weight percent unless specified otherwise.

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precipitated at grain boundaries and within grains on the alloy surface both exceeded the critical amount required for lateral growth of the Cr_2O_3 particles and the surfaces of these alloys were completely covered with a continuous, external layer of Cr_2O_3 during oxidation. However, in the case of alloys with chromium concentrations between approximately 5 to 30 pct, the volume fraction of precipitated Cr_2O_3 exceeded the critical value required for external scale formation only at grain boundaries but not within the interior of the grains. Consequently, the surfaces of these alloys had external scales of Cr_2O_3 over the grain boundaries but internal Cr_2O_3 subscales with external scales of NiO away from the grain boundaries. Under these latter conditions, it was found that chromium could diffuse laterally in the alloy from those areas covered with an external layer of Cr_2O_3, *i.e.*, grain boundaries, to areas where the Cr_2O_3 was present as a subscale. This diffusion of chromium resulted in an increase in the volume fraction of Cr_2O_3 precipitated in the subscale zone and continuous layers of Cr_2O_3 could be formed at the subscale front in these regions. For the alloys used in the previous studies,[1] continuous layers of Cr_2O_3 were formed on Ni-20Cr alloys in the subscale regions after approximately 30 hr of oxidation at 900°C. For shorter periods of oxidation, the Cr_2O_3 layer was semicontinuous with the continuous portion at the subscale front emanating from points where the Cr_2O_3 had been formed as an external scale over alloy

C. S. GIGGINS and F. S. PETTIT, Member AIME, are Senior Research Assistant and Senior Research Associate, respectively, Advanced Materials Research and Development Laboratory, Pratt & Whitney Aircraft, Division of United Aircraft Corporation, Middletown, Conn. Manuscript submitted May 8, 1969. IMD

grain boundaries. Some lateral growth of a Cr_2O_3 layer in the subscale region was observed on Ni-15Cr and even Ni-10Cr alloys but this layer was never continuous after 30 hr of oxidation.

These results indicate that the selective oxidation of chromium in Ni-Cr alloys with chromium contents between 5 to 30 pct may be dependent upon the grain size of the alloy. Fine-grained specimens in this compositional range should have a larger fraction of the surface covered with external Cr_2O_3 than coarse-grained specimens and the subscale areas required to be sealed via lateral diffusion of chromium should be smaller. It is therefore to be expected that a continuous layer of Cr_2O_3 can be formed on alloys in this compositional range after short periods of oxidation providing the alloy grain-size is sufficiently small.

Some studies[2,3] have established that the oxidation behavior of alloys can be significantly influenced by pretreatments which produce mechanically deformed surfaces. It has been found that deformed surfaces usually promote the selective oxidation of elements in alloys and it is believed that these effects are due to rapid diffusion of elements in the deformed layer. In view of the previous results,[1] which showed that alloy grain boundaries may play an important role in the selective oxidation of chromium in Ni-Cr alloys, deformed surfaces may promote the selective oxidation of elements in alloys as a result of the numerous grain boundaries formed on the alloy surfaces via recrystallization during heating to the oxidation temperature. The purpose of the present studies was to determine the effect of alloy grain size and surface deformation on the selective oxidation of chromium in Ni-Cr alloys at temperatures of 900° and 1100°C in 0.1 atm of oxygen.

EXPERIMENTAL

The average grain diameter of the alloys used in the previous studies[1] was not less than 0.04 mm and alloys with compositions between 5 and 30 pct chromium had average grain diameters between 0.04 and 0.14 mm. Since the oxidation kinetics were already available for these relatively coarse-grained alloys, it was desirable to use these same alloys in the present studies. The surfaces of the alloys listed in Table I of the previous paper were deformed by using a Model F S.S. White Industrial Airbrasive Unit, which delivered a controlled mixture of 25 μ Al_2O_3 particles in a stream of dry air at high velocity against the surface of a specimen. The amount of surface deformation produced by this treatment was not determined but a recrystallized layer about 15 μ thick was formed upon annealing deformed specimens.

The grain size at the surface of the specimens was reduced to an average grain diameter of 0.01 mm by annealing the deformed specimens, *i.e.*, grit-blasted,

for 2 hr at 900°C in vacuum. The structures of a typical specimen before and after the deformation-annealing treatment are compared in Fig. 1. The fine grains on the surface of grit-blasted-annealed specimens were very stable at 900°C and the grain diameter was virtually unchanged even after a 20-hr anneal at this temperature. At 1100°C grain growth was quite rapid and the average grain diameter eventually exceeded 0.01 mm. Consequently, stress-free, fine-grained specimens were tested at 900°C and alloys with deformed surface layers were tested at 900° and 1100°C.

The apparatus used in the oxidation experiments, experimental procedure, e.g., specimen size, cleaning of specimens, and so forth, and techniques used to examine oxidized specimens were the same as those described in the preceding paper.[1]

RESULTS

Weight-Change Measurements. Typical curves obtained from weight-change vs time measurements for grit-blasted and grit-blasted-annealed specimens are presented in Figs. 2 and 3 for temperatures of 900° and 1100°C, respectively. The data for all specimens eventually followed a parabolic rate law although the oxidation kinetics frequently deviated from such a relationship during the early stages of oxidation. In Fig. 4 the parabolic rate constants obtained for grit-blasted and grit-blasted-annealed specimens are compared to the rate constants obtained for electropolished, coarse-grained samples. The results presented in this figure for experiments performed at 900°C show that the rate constants obtained for grit-blasted and grit-blasted-annealed specimens are similar but significantly less than the parabolic rate constants obtained for electropolished, coarse-grained specimens. At 1100°C the grit-blasted specimens oxidized at slower rates than specimens of the same composition in the stress-free, electropolished condition.

Examination of Oxidized Specimens. The microstructure of grit-blasted and grit-blasted-annealed specimens were identical after oxidation in 0.1 atm of oxygen at 900°C. Alloys with these surface preparations and containing 10 pct or more chromium, developed thin, external oxide scales during oxidation
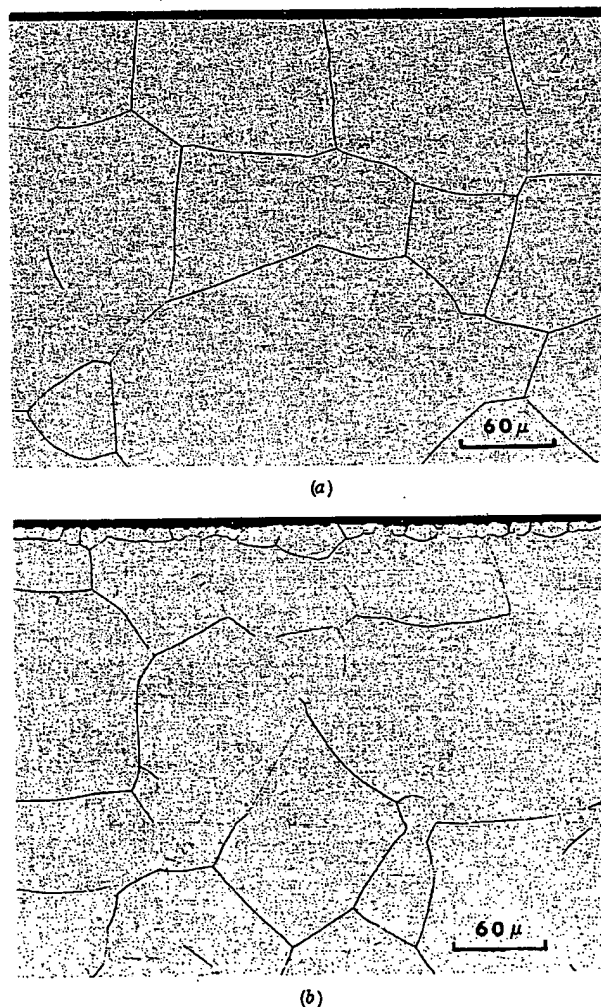

(a)

(b)

Fig. 1—Effect of surface pretreatment on a Ni-15Cr alloy heat treated for 2 hr in vacuum at 900°C. (a) Electropolished surface. (b) Grit-blasted surface. Etchant: 30 ml H₃PO₄, 170 ml H₂O, Electrolytic, Pt-Pt (2 v for ~30 sec).
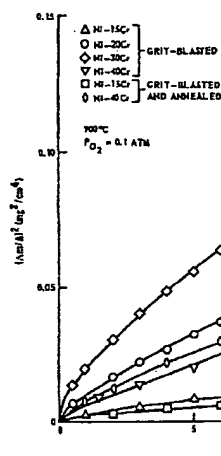

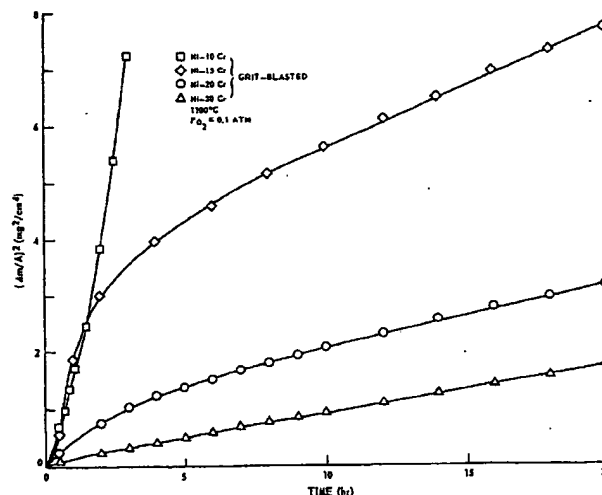Fig. 2—Typical oxidation data for grit-blasted and grit-blasted-annealed Ni-Cr alloys at 900°C.

Fig. 3—Typical oxidation data for grit-blasted Ni-Cr alloys at 1100°C.

as shown in Fig. 5. X-ray diffraction analyses of these oxide scales showed that Cr_2O_3 was the principal phase. $NiCr_2O_4$ was also detected but the intensity of diffraction lines for this phase were quite weak indicating that it was probably formed during the initial stages of oxidation before a continuous layer of Cr_2O_3 could be developed. The oxidation attack of alloys with grit-blasted or grit-blasted-annealed pretreatments was not uniform when the alloy contained less than 10 pct Cr and occasionally the oxidation rates of alloys in this compositional range were observed to increase with time as shown in Fig. 4. The microstructure of a typical specimen is presented in Fig. 6. Some portions of the surface are covered with a thin layer of Cr_2O_3 while other portions have an external scale of NiO with a Cr_2O_3 subscale. It is evident that the chromium was not selectively oxidized uniformly over the entire specimen surface. On the coarser grained alloys, i.e., electropolished specimens, external scales of Cr_2O_3 were observed on specimens with 30 pct or more Cr while substantial amounts of NiO were found on alloys with smaller chromium contents. Specimens of electropolished and grit-blasted Ni-10Cr which were oxidized at 900°C are compared in Fig. 7. A thick, external scale of NiO with a subscale of Cr_2O_3 has been formed on the electropolished specimen whereas a thin, external scale of Cr_2O_3 is present on the grit-blasted specimen. In this photograph the Cr_2O_3 is barely visible on the grit-blasted specimen but the zone of small grains at the specimen surface are easily discernible. The results obtained at 900°C

show that the chromium content above which continuous external scales of Cr_2O_3 are formed on Ni-Cr alloys has been reduced from 30 to 10 pct by the grit-blasting or grit-blasting-annealing treatments.

At 1100°C thin, external oxide scales were formed on grit-blasted specimens during oxidation when the alloy contained 30 pct or more Cr. X-ray diffraction analysis of these oxide scales showed that Cr_2O_3 was the principal phase in the scale. Trace amounts of $NiCr_2O_4$ were also observed in the scales. Oxidized specimens of grit-blasted Ni-20Cr and Ni-15Cr alloys exhibited a continuous layer of Cr_2O_3 on the alloy surface, however, at some areas the Cr_2O_3 layer had formed beneath a layer of NiO as shown in Fig. 8(a). The Ni-20Cr specimens had fewer of these areas, i.e., Cr_2O_3 beneath NiO, than the Ni-15Cr samples. The oxidation attack of grit-blasted specimens containing less than 15 pct Cr was not uniform as shown in Fig. 9. It can be seen that on some areas of the alloy surface an external layer of Cr_2O_3 has been formed while in other areas external scales of NiO with Cr_2O_3 subscales

Fig. 5—Microstructure of a grit-blasted Ni-20Cr alloy after 65 hr of oxidation at 900°C in 0.1 atm of oxygen. An external scale of Cr_2O_3 has been formed.

Fig. 6—Microstructure of a grit-blasted Ni-5Cr alloy after 19 hr of oxidation at 900°C in 0.1 atm of oxygen. The oxidation attack is not uniform. In some areas a thin external scale of Cr_2O_3 is visible while in other areas NiO with Cr_2O_3 subscales are evident.
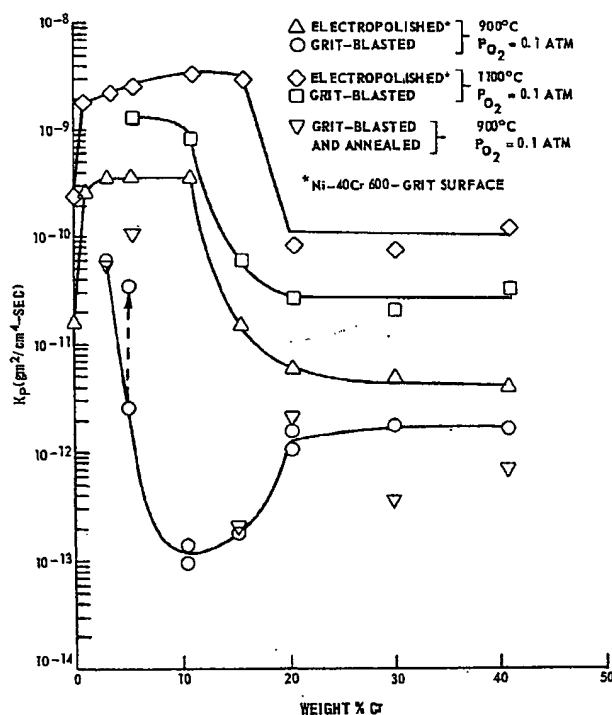

Fig. 4—Composition dependence of the parabolic rate constants for the oxidation of electropolished, 600-grit for Ni-40Cr, and grit-blasted nickel-chromium alloys at 900° and 1100°C. Data for grit-blasted-annealed alloys oxidized at 900°C are also included. (The kinetic data for the grit-blasted Ni-5Cr alloy exhibited two parabolic regions with the larger rate constant occurring at the later times.)
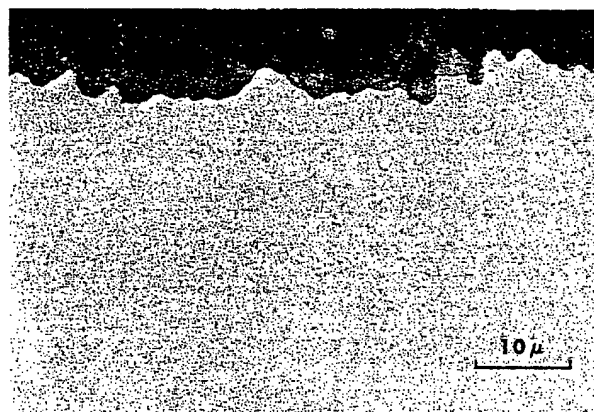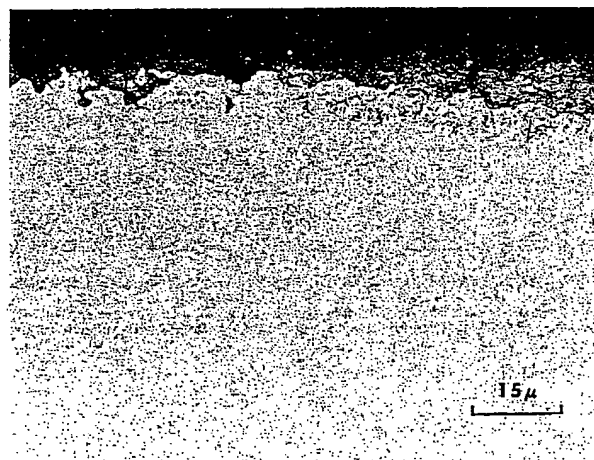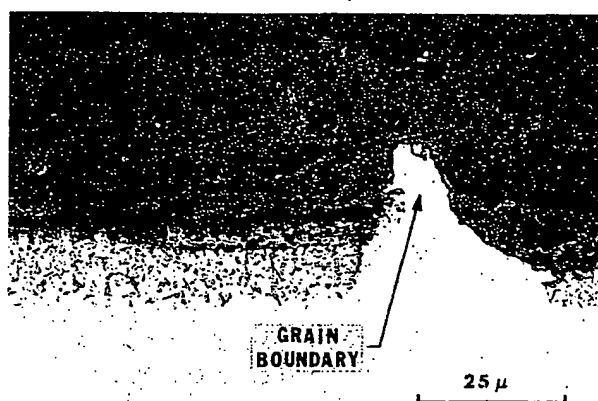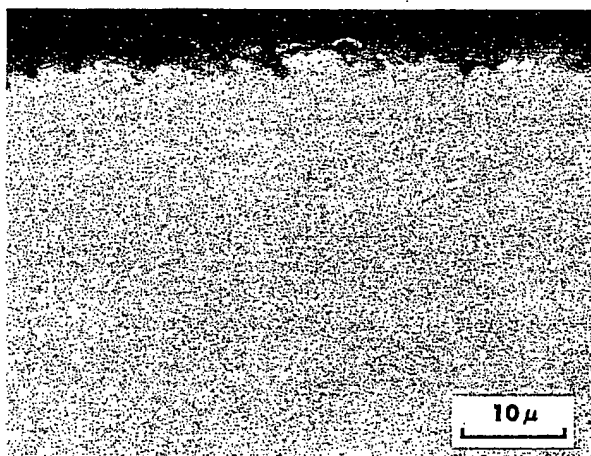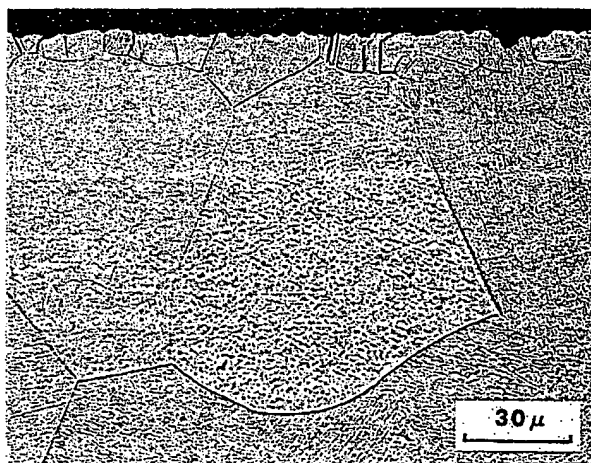
(a)

(b)

(c)

Fig. 7—Effect of surface pretreatment on a Ni–10Cr alloy oxidized for 20 hr in 0.1 atm of oxygen at 900°C. (a) Electropolished surface. A two-zoned layer of NiO and a Cr_2O_3 subscale has been formed. Some lateral growth of the Cr_2O_3 scale is evident at a grain boundary. (b) Grit-blasted surface. An external scale of Cr_2O_3 which is barely discernible has been formed. (c) Specimen described in (b) in etched condition. Note the small grains which were formed by recrystallization of the deformed surface layer. Etchant: Aged solution of 30 ml Lactic acid, 20 ml Acetic acid, 30 ml HCl, 10 ml HNO_3. Immersion.

are evident. The microstructure of oxidized, electropolished, coarse-grained specimens was identical to that of grit-blasted samples when the alloy contained 30 pct or more Cr. In the case of the oxidation of electropolished specimens, containing less than 30 pct Cr, external scales of NiO with Cr_2O_3 subscales were formed. In the Cr_2O_3 subscale zone, a continuous layer of Cr_2O_3 was observed on the Ni-20Cr alloy after approximately 30 hr of oxidation but no continuous Cr_2O_3 layer was observed on alloys with smaller chromium contents. In Figs. 8(a) and (b) oxidized specimens of a grit-blasted and an electropolished Ni-15Cr alloy are compared. The grit-blasted specimen has a continuous layer of Cr_2O_3 whereas a Cr_2O_3 subscale has been formed on the electropolished specimen. The results obtained at 1100°C also show that the selective oxidation of chromium has been promoted by the grit-blasting treatment.

Experiments Using CO-CO$_2$ Gas Mixtures. To examine the behavior of a Ni-Cr alloy with different surface preparations, under conditions where NiO
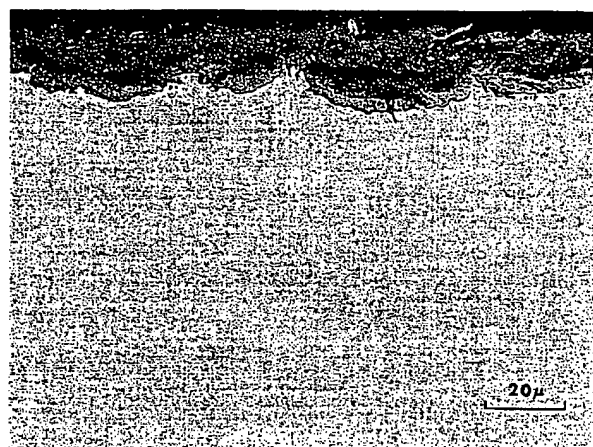
(a)
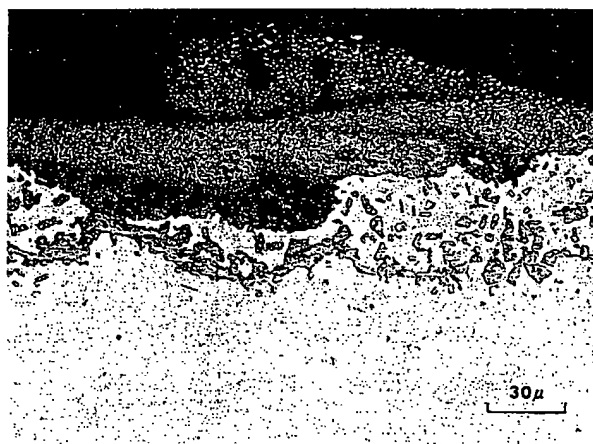
(b)

Fig. 8—Comparison of the oxide scales formed on grit-blasted and electropolished specimens of Ni-15Cr after oxidation at 1100°C in 0.1 atm of oxygen. (a) Grit-blasted surface. A continuous layer of Cr_2O_3 has formed beneath a layer of NiO. (b) Electropolished surface. The chromium has been oxidized internally and appears as a subscale beneath the NiO layer.

was not stable, a Ni-10Cr alloy with an average grain diameter of about 0.1 mm was electropolished and then one-half of the surface was grit-blasted. This specimen was then oxidized in a CO-CO$_2$ mixture with CO/CO$_2$ = 0.07 at 900°C. The surface of this oxidized specimen is shown in Fig. 10(a) which shows that an external scale of Cr$_2$O$_3$ has been formed on the grit-blasted portion of the surface while on the coarse-grained, electropolished area Cr$_2$O$_3$ has been formed only at grain boundaries. A cross-sectional view of this specimen is presented in Fig. 10(b). It is evident that the chromium has been oxidized externally over the grit-blasted area but internally over the electro-polished surface. Similar results were obtained when such a specimen was annealed in vacuum after the grit-blasting treatment prior to the oxidation reaction.

DISCUSSION OF RESULTS

The results obtained with grit-blasted and grit-blasted-annealed specimens at 900°C were similar. The annealed alloys were known to have a thin layer of fine, stress-free grains on their surfaces during the entire period of oxidation and the grit-blasted alloys were found to have similar structures when examined after oxidation. It therefore appears that the deformation introduced during the grit-blasting treatment affects the oxidation behavior of Ni-Cr alloys by producing numerous grain boundaries on the alloy surface via the recrystallization which occurs as the specimen is heated to the test temperature.

The results presented in Fig. 4 show that at both 900° and 1100°C the oxidation rates of all Ni-Cr alloys with fine grains, i.e., grit-blasted or grit-blasted-annealed, are smaller than the oxidation rates of alloys with the same composition but which have coarser grains at their surfaces, i.e., electropolished. However, the microstructure of oxidized specimens was found to be dependent upon the alloy grain size only when the alloy contained less than 30 pct Cr, see Figs. 7 and 8. In view of this condition it is convenient to discuss the behavior of alloys containing less than 30 pct Cr first and then proceed to the alloys with larger chromium concentrations.

Alloys With Less than 30 pct Cr. The results obtained in the present studies show that continuous, external scales of Cr$_2$O$_3$ are formed on the fine-grained Ni-Cr alloys at lower chromium concentrations than on the coarse-grained alloys. This difference in behavior is believed to result from the larger number of grain boundaries that are present on the surfaces of the fine-grained alloys. During the early stages of oxidation of a Ni-Cr alloy with less than 30 pct Cr, chromium is oxidized externally at alloy grain boundaries but internally at other areas on the alloy surface. When the alloy has a small grain size, i.e., ≤0.01 mm, the Cr$_2$O$_3$ in the subscale region becomes continuous as a result of the lateral diffusion of chromium to the subscale front from those areas where Cr$_2$O$_3$ exists as a continuous layer. As the alloy grain size is increased the chromium content of the alloy must also be increased before a continuous layer of Cr$_2$O$_3$ will be formed in the subscale region since the larger diffusion distances result in a smaller increase in the volume fraction of precipitated Cr$_2$O$_3$ due to lateral diffusion of chromium.

The smaller oxidation rates of fine-grained alloys compared to those for coarse-grained alloys are a result of the increased selective oxidation of chromium
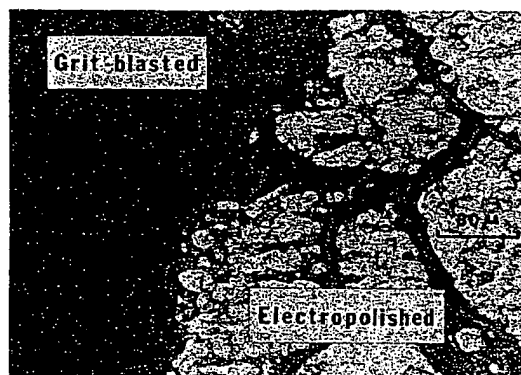
(a)

(b)

Fig. 10—Effect of surface pretreatment on a Ni-10Cr alloy oxidized for 20 hr in a CO-CO$_2$ mixture (CO/CO$_2$ = 0.07) at 900°C. Prior to oxidation one-half of the surface was electropolished and the other half was grit-blasted. Chromium has been oxidized externally on the grit-blasted surface but internally in the electropolished area except at alloy grain boundaries where it has also been oxidized externally. (a) Surface topography. (b) Transverse section.
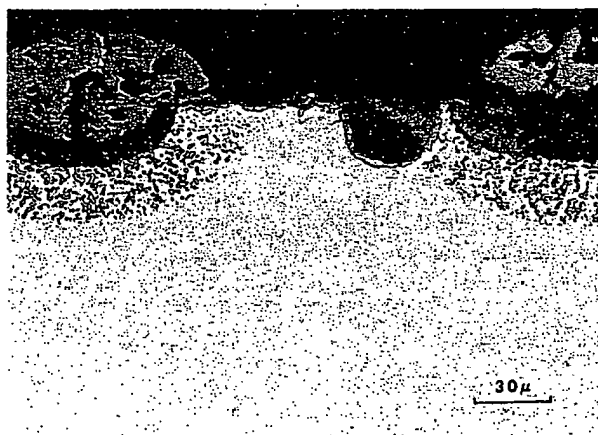

Fig. 9—Microstructure of a grit-blasted Ni-10Cr alloy after 20 hr of oxidation at 1100°C in 0.1 atm of oxygen. The oxidation attack is not uniform. In some areas a thin external scale of Cr$_2$O$_3$ is visible while in other areas clumps of NiO with Cr$_2$O$_3$ subscales are evident.

for fine-grained alloys. External scales of Cr_2O_3 are formed on fine-grained alloys during oxidation while substantial amounts of NiO are formed on the surfaces of coarse-grained alloys with the same bulk composition. Since transport through Cr_2O_3 is slower than transport through NiO, the fine-grained alloys therefore have smaller oxidation rates than the coarse-grained alloys. Examination of Fig. 4 shows that the parabolic rate constants for fine-grained alloys are dependent upon the chromium content of the alloy. Below 10 pct Cr at 900°C and below 20 pct Cr at 1100°C the oxidation rates of fine-grained alloys begin to increase and have poor reproducibility because continuous external Cr_2O_3 scales are not formed over the entire surface and NiO is formed in some areas as shown in Figs. 6 and 9. Smaller chromium contents are sufficient for selective oxidation at 900°C because smaller grains are formed in the recrystallized layers than at 1100°C. The oxidation rates of these alloys are still smaller than those of coarse-grained alloys with similar compositions since uniform external scales of NiO and Cr_2O_3 subscales are formed on coarse-grained alloys. The nonuniform oxidation of fine-grained alloys is believed to result from local variations in the grain size on the surfaces of the alloys which indicates that continuous, external scales of Cr_2O_3 may form on alloys with lower chromium concentrations than those determined in the present studies providing the alloy grain size can be made smaller than that of the fine-grained alloys used in the present experiments.

At 900°C the parabolic rate constants for fine-grained alloys increase with alloy chromium content from 10 to 20 pct Cr and are constant for larger chromium concentrations. The dependence of the parabolic rate constants on the chromium content of the alloy when Cr_2O_3 is the only oxide formed upon the alloy surface has been discussed in the preceding paper.[1] It can be shown that the parabolic rate constants for fine-grained alloys at 900°C should increase with chromium content up to about 19 pct Cr and then become constant. The data in Fig. 4 for 900°C are consistent with these considerations. A similar effect is not observed at 1100°C because even though a continuous layer of Cr_2O_3 has been found on alloys with 15 and 20 pct Cr, substantial amounts of NiO were formed before the Cr_2O_3 scale became continuous, see Fig. 8. The formation of NiO results in an abrupt increase of the weight-gain vs time curves during the early stages of oxidation which causes the parabolic rate constants calculated from these data to be larger than those for the growth of Cr_2O_3.

Alloys With Greater than 30 pct Cr. At both temperatures the parabolic rate constants for alloys containing 30 pct or more Cr are independent of the bulk chromium content of the alloy. This is to be expected for the growth of Cr_2O_3 scales on alloys with large chromium concentrations. At both temperatures the parabolic rate constants of fine-grained specimens

are smaller than those of coarse-grained samples. In the case of alloys with these chromium contents, both fine and coarse-grained specimens formed external layers of Cr_2O_3 virtually at the onset of oxidation. The rate constants for fine-grained or deformed specimens were about a factor of three smaller than those for electropolished specimens which were oxidized under similar conditions. This difference is not large; however, since these fine-grained or grit-blasted specimens were always observed to oxidize slower than electropolished specimens, it is believed to be a true effect. Factors such as modification of the oxide scale on account of the electropolishing treatment,[4] surface area changes and contamination of the surfaces of grit-blasted specimens with the abrasive material were found to have negligible effects on the parabolic rate constants of these alloys. The results can be explained if one assumes that short circuit diffusion paths are present in the Cr_2O_3 formed on the electropolished specimens or that void formation occurs at the Cr_2O_3-alloy interface on grit-blasted specimens. However, such assumptions are speculation at this time and an explanation for the decreased parabolic rate constants for grit-blasted or fine-grained alloys which contained 30 pct or more Cr is not available.

SUMMARY AND CONCLUDING REMARKS

The oxidation properties of Ni-Cr alloys with fine grains, coarse grains, and deformed surface layers have been compared. The behavior of alloys with fine grains and with deformed surface layers has been found to be the same and it has been concluded that deformed surfaces affect the oxidation properties of Ni-Cr alloys at temperatures of 900° and 1100°C by producing fine grains via recrystallization of the cold worked layer as the specimen is heated to the oxidation temperature. The oxidation properties of Ni-Cr alloys with chromium concentrations between 10 and 30 pct have been found to be dependent upon the grain size of the alloy. This effect is caused by the selective oxidation of chromium at alloy grain boundaries over this compositional range.

ACKNOWLEDGMENTS

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